PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-157827**

(43)Date of publication of application : **15.06.1999**

(51)Int.CI. C01B 33/193
B01J 21/08
G01N 30/48
// B01J 20/10
B01J 32/00
C12H 1/04

(21)Application number : **09-338077**

(22)Date of filing : **21.11.1997**

(71)Applicant : **SHIONOGI & CO LTD**

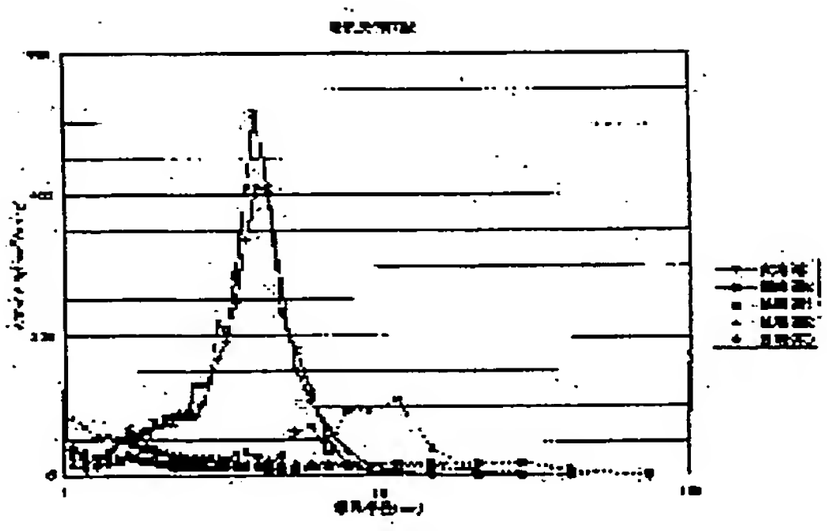
(72)Inventor : **CHIKAKI YASUTAKA**
AOKI TSUNETO

(54) NEW SILICON DIOXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a silicon dioxide having excellent performance as an adsorbent, filler or the like.

SOLUTION: In the distribution curve of pores of the silicon dioxide, the max. value of $\Delta Vp/\Delta Rp$ (wherein Vp is the pore volume and Rp is the pore radius) is present in the region of <10 nm pore radius, the max. $\Delta Vp/\Delta Rp$ is ≥100 mm3/nmg, and the proportion of the pore volume corresponding to the range of the peak radius (the pore radius at the max. $\Delta Vp/\Delta Rp$)±1 nm is ≥20% of the whole pore volume.



LEGAL STATUS

[Date of request for examination] 09.11.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

Machine Translation of JP-Application No. H09-338077

[Field of the Invention] This invention relates to the new silicon dioxide adsorbed and held alternatively to the magnitude of an adsorbed [/] maintenance component, when it is used as a food-grade adsorbent, the bulking agent for chromatography, catalyst support, the bulking agent for papers, etc.

[Description of the Prior Art] Conventionally, the silicon dioxide is used widely from the magnitude of the specific surface area, and the magnitude of pore volume for the application of a drying agent, an adsorption purification agent, the bulking agent for chromatography, catalyst support, the bulking agent for papers, etc. The pore structure of a silicon dioxide is decided by the magnitude of a primary particle, and condensation extent, and the silicon dioxide with the pore structure suitable for each application is used. As a technique about the above-mentioned application, the bulking agent for the ink jet recording papers etc. is known, for example as an adsorption purification agent as the remover of muddiness components, such as playback of edible oil, Biel, wine, and sake, and a bulking agent for special papers.

[0003] In the technique about the above-mentioned application, specific surface area, pore volume, and average pore size are mainly specified as physical properties in connection with the pore structure of a silicon dioxide.

[0004] For example, as an adsorption purification agent for Biel, the silicon dioxide of the shape of the shape of the thin film integrated circuit 0.2 - 1.5 ml/g and whose specific surface area 5-100 micrometers and pore volume are 100-1000m2/g for particle size, and a scale, and a rod is indicated in JP,5-177132,A. Moreover, the approach specific surface area carries out contact processing of the silica gel 0.3 - 2.0 ml/g and whose average pore diameter 300-800m2/g and pore volume are 20-150A in JP,62-100597,A as a regenerant of edible oil as the playback approach of the edible oil which deteriorated is indicated. Thus, there is much what has specified specific surface area, pore volume, and average pore size also in which application.

[0005] However, in average pore size, the configuration of pore distribution did not become clear, consequently even if it was the physical-properties value of the above-mentioned range, what does not discover the engine performance enough was contained.

[0006] On the other hand, it is indicated that using a silicon-dioxide porous body for JP,9-143461,A as an accumulation agent is indicated as a technique about the sharpness of pore distribution of a silicon dioxide, the pore of a porous body is in the range whose main pore diameter which shows the maximum peak in a pore distribution curve is 1-10nm, and 60 - 100% of the pore volume of a porous body is within the limits of **40% of main pore diameters. However, with this technique, there is no publication of the range of pore volume.

[0007] Moreover, the manufacture approach that it is the manufacture approach of silica gel of making the range of desired carrying out change control of a BET specific surface area, pore volume, and the average pore size, and silica gel with sharp pore distribution can be obtained is indicated by JP,9-30809,A. Furthermore, although it is indicated that less than 0.5 silica gel is preferably obtained for B/A 0.6 or less if the median size of the peak in pore volume distribution is set to A and half-value width is set to B, the range of a controllable specific surface area, pore volume, and a median size is not specified.

[0008] The purpose of this invention is to offer the silicon dioxide which has the outstanding adsorption engine performance exceeding the silicon dioxide of the above-mentioned conventional technique, and has a high property as an adsorbent and a bulking agent.

[0009]
[The means for solving a technical problem and the gestalt of implementation of invention] In order that this invention persons may attain the above-mentioned purpose, as a result of repeating examination wholeheartedly, it sets for the reaction of an alkali-metal silicate water solution and a mineral acid. The silicon dioxide obtained in some conditions which made silicic-acid concentration in an alkali-metal silicate water solution below 10 weight / capacity (w/v) % sets to a pore distribution curve. 10nm or less of pore radii -- a delta ****/delta Rp value (however, **** -- pore volume --) Rp has the maximum of a pore radius and the maximum of the delta ****/delta Rp value is more than 100mm3/nm-g. And the percentage of the pore volume which is equivalent to the pore peak radius (pore radius delta ****/delta Rp indicates maximum to be) of **1nm to total pore volume is 20% or more, and the knowledge of the engine performance which was excellent when the silicon dioxide which shows this description used it as an adsorbent and a bulking agent being shown was carried out.

[0010] Namely, the silicon dioxide concerning this invention is set to a pore distribution curve, though it is the silicon dioxide which has the general physical-properties value which specific surface area calls 300-500m2/g, and

pore volume calls 0.8 - 1.4 ml/g. It has the maximum of a delta ****/delta Rp value to the field of 10nm or less of pore radii, and has the description that the delta ****/delta Rp value of the maximum is more than 100mm3/nm-g, and the percentage of the pore volume which is equivalent to the pore peak radius of **1nm to total pore volume is 20% or more. This description shows that pore distribution is sharp, and shows the engine performance which was excellent when it used as an adsorbent and a bulking agent.

[0011] Hereafter, it explains in more detail about this invention. The silicon dioxide of this invention is a silicon dioxide which has the maximum of a delta ****/delta Rp value in the range of 10nm or less of pore radii, and has the description that the delta ****/delta Rp value of the maximum is more than 100mm3/nm-g, and the percentage of the pore volume which is equivalent to the pore peak radius of **1nm to total pore volume is 20% or more in a pore distribution curve.

[0012] It is important when it attains the purpose of this invention that the maximum of a delta ****/delta Rp value is in 10nm or less of pore radii here. If the maximum of a delta ****/delta Rp value is in the place exceeding 10nm, the engine performance in the case of using as an adsorbent of high polymers, such as protein, especially will fall. The maximum of a delta ****/delta Rp value is more preferably good for there to be 3-8nm in the range of 3-5nm still more preferably. In this case, as for the maximum of delta ****/delta Rp, it is desirable that it is in the place exceeding 3nm.

[0013] Next, the delta ****/delta Rp value of the maximum of the silicon dioxide of this invention is more than 100mm3/nm-g. The pore volume of the case of under 100mm3/nm-g of this pore-radius range decreases, sharpness is spoiled, the selectivity of adsorption falls, or even if selectivity is maintained, the amount of adsorption falls. The delta ****/delta Rp value of maximum is more than 400mm3/nm-g still more preferably more than 200mm3/nm-g more preferably.

[0014] Furthermore, the percentage of pore volume that the silicon dioxide of this invention is equivalent to the pore peak radius of **1nm to total pore volume is 40% or more more preferably 20% or more. The sharpness of pore distribution is spoiled by less than 20% of case, and the selectivity of adsorption falls.

[0015] The specific surface area in the nitrogen adsorption process by the BET adsorption method is 300-500m2/g, and, as for the silicon dioxide of this invention, it is desirable that pore volume is 0.8 - 1.4 ml/g. If specific surface area generally becomes small in a silicon dioxide, pore size and pore volume will become large, and pore distribution will tend to become broadcloth. Moreover, if specific surface area becomes large, pore volume will become small and pore distribution will tend to become Sharp. Therefore, although pore distribution will become Sharp more if the case of under 300m2/g has a possibility that the sharpness of pore distribution may be spoiled and 500m2/g is exceeded, pore volume becomes small and there is a possibility that the amount of adsorption may fall.

[0016] Moreover, as for the silicon dioxide of this invention, it is desirable that 1-30 micrometers of the mean particle diameter are 5-20 micrometers more preferably. If the case where it becomes difficult to remove the silicon dioxide itself arises and it exceeds 30 micrometers when mean particle diameter is less than 1 micrometer, and it is used as an adsorbent, the case where the adsorption engine performance falls will arise.

[0017] Furthermore, as for the silicon dioxide of this invention, it is desirable that oil absorption is 150ml / 100g or more. When it is used as a bulking agent for papers, oil absorption is required for maintenance of the moisture and water soluble polymer which are a medium, and the case where engine performance sufficient in 150ml / less than 100g is not expectable produces it.

[0018] Furthermore, as for especially the silicon dioxide of this invention, it is desirable that pH of a 5-% of the weight slurry is 4-8 eight or less. When pH is higher than 8, there is a possibility of bringing about the fall of specific surface area and increase of a pore peak radius by aging.

[0019] The silicon dioxide concerning this invention can be obtained by the approach according to the so-called process of the wet method silica by neutralization with an alkali-metal silicate water solution and a mineral acid. in this case, the silicic-acid concentration in an alkali-metal silicate water solution -- 10 -- w/v % or less of things more preferably reacted as 2 - 8 w/v% is recommended.

[0020] As an alkali-metal silicate, it is desirable to use a No. 3 sodium silicate from an economical standpoint. Moreover, a sulfuric acid and a hydrochloric acid are desirable from an economical standpoint the same as a mineral acid. The concentration of a mineral acid has six to 16 desirable convention.

[0021] The above-mentioned alkali-metal silicate water solution is warmed, and the sulfuric acid of predetermined concentration is added. The temperature at the time of addition has desirable 50-100 degrees C. As long as it is required, a sulfuric acid may be divided into several times and you may add. 80 - 95% of the last neutralization

index is desirable. If required, it can heat at 80 degrees C or more after addition termination of a sulfuric acid. As for especially after reaction termination, it is desirable to lower pH to 3-5 5.5 or less.

[0022] As for the obtained silicon-dioxide slurry, it is desirable to readjust pH to especially 3-5 5.5 or less while filtering and washing this and re-distributing in water. Then, a silicon dioxide can be obtained by filtration, washing, and desiccation, and the silicon dioxide of predetermined grain size can be further obtained by grinding and the classification.

[0023] The silicon dioxide of this invention can be used for the application for which the silicon dioxide is used conventionally, and is especially suitable as an adsorbent, catalyst support, and a bulking agent. As an adsorbent, it can be used as purification agents, such as edible oil, Biel, and wine, etc., and is effective also as the bulking agent for chromatography, a bulking agent for papers, etc. In this case, the silicon dioxide of this invention has the specific adsorption engine performance to the matter which has with a molecular weight of about 25000 to 50000 molecular weight, especially protein.

[0024]
[Effect of the Invention] The silicon dioxide of this invention has the engine performance which was excellent as an adsorbent, a bulking agent, etc.

[0025]
[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, in the following example, the physical-properties measuring method of a silicon dioxide and the measuring method of the adsorption property over protein are as follows.

[0026] Particle size distribution were measured using the 100-micrometer aperture with the Coulter counter TA-II mold grain-size measuring device made from physical-properties Measuring method [Mean-particle-diameter] Coal tar of a silicon dioxide, and the median size (diameter of 50%) was made into mean particle diameter.
Once having distributed 100ml of ion exchange water and boiling 5g of [Product pH] samples, it cooled to the room temperature and pH of a slurry was measured.
It measured with the nitrogen adsorption process (BET adsorption method) using the full automatic specific surface area made from [Specific-surface-area] Japan Bell / pore distribution measuring device (BELSORP28). In addition, the vacuum deairing of the pretreatment of a sample was carried out at 160 degrees C for 2 hours. (Bibliography: S.Brunauer, P.H.Emmett, E.Teller, J.Amer.Chem.Soc., 60,309 (1938))
[Pore volume] Using the above-mentioned BELSORP28, it asked for the adsorption isotherm of nitrogen and asked for the pore volume of 1-100nm of pore radii with the analysis method of a DORIMOA heel based on JIS-K1150. This numeric value was made into total pore volume. Moreover, it asked for the pore volume of the range of **1nm pore peak radius from the curve which plotted the integral value over the pore radius by this approach.
[Pore distribution] Pore distribution was measured with the nitrogen adsorption process using the above-mentioned BELSORP28. Count of pore distribution analyzed by the approach (D. Dollimore, G.R.Heal, J.Appl.Chem., 14,109 (1964)) of a DORIMOA heel. In addition, the vacuum deairing of the pretreatment of a sample was carried out at 160 degrees C for 2 hours.
It asked from the pore distribution map of each sample shown in [pore peak radius] drawing 1 . It is the pore radius which shows the maximum of delta ****/delta Rp.
[Average pore radius]
Average pore radius (nm)
= 2000x (pore volume (ml/g)/specific surface area (m2/g))
It computed more.
It measured by the approach of [oil absorption] JIS-K -5101.
[Proteinic adsorption property] protein was dissolved in the 10 v/v% ethanol water solution, and the solution of 100 ppm of protein was prepared. In this liquid, 500 ppm added and the silicon dioxide was agitated for 20 minutes. The absorbance in 280nm was measured after filtration. The used protein is a trypsin inhibitor (molecular weight 20100), cull BONIKKUANHAIDORAZE (molecular weight 30000), cow serum albumin (molecular weight 69000), and a catalase (molecular weight 230000). Surface coverage was computed from the following formulas.
The result of each sample is shown in surface coverage =100-[(absorbance of silicon-dioxide processing liquid)/(absorbance of silicon-dioxide unsettled liquid)] x100, in addition drawing 2 .

[0027] [Example 1] Silicic-acid concentration warmed No. 3 sodium-silicate water-solution 75L which is 6 w/v% at 60 degrees C, and added sulfuric-acid 2.4L of 12 normality under churning. Next, it agitated for 30 minutes and 0.70L addition of the sulfuric acid of 12 normality was done. It heated at 60 degrees C for 10 more minutes. Next, 0.53L addition of the sulfuric acid of 12 normality was done, and it was heated at 60 degrees C for 30 more minutes. After adjusting pH to 4.0, the slurry was filtered and washed and it re-distributed in water. After readjusting pH to

4.0, it filtered and washed and the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification. The physical-properties value of the obtained silica and the proteinic adsorption property were shown in Table 1.

[0028] [Example 2] Silicic-acid concentration warmed No. 3 sodium-silicate water-solution 75L which is 5 w/v% at 70 degrees C, and added sulfuric-acid 2.0L of 12 normality under churning. Next, it agitated for 30 minutes and 1.0L addition of the sulfuric acid of 12 normality was done. It heated for 30 more minutes. After adjusting pH to 4.0, the slurry was filtered and washed and it re-distributed in water. After readjusting pH to 4.0, it filtered and washed and the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification. The physical-properties value of the obtained silica and the proteinic adsorption property were shown in Table 1.

[0029] [Example 1 of a comparison] Silicic-acid concentration warmed No. 3 sodium-silicate water-solution 50L which is 11 w/v% at 60 degrees C, and poured sulfuric-acid 2.1L of 12 normality under churning. After agitating for 30 more minutes, the temperature up was carried out to 90 degrees C. Sulfuric-acid 2.3L of 12 normality was poured again. It agitated for 30 minutes at 95 more degrees C after pouring termination. After adjusting pH to 4.0, it filtered and washed and re-distributed in water. After readjusting pH to 4.0, the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification. The physical-properties value of the obtained silica and the proteinic adsorption property were shown in Table 1.

[0030] [Example 2 of a comparison] After silicic-acid concentration added 2.5kg of sodium sulfates to No. 3 sodium-silicate water-solution 50L which is 7 w/v%, it warmed at 40 degrees C and sulfuric-acid 0.8L of 12 normality was poured under churning. After agitating for 30 more minutes, sulfuric-acid 1.6L of 12 normality was poured again. After pouring termination, it filtered and washed and re-distributed in water. After readjusting pH to 4.0, the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification. The physical-properties value of the obtained silica and the proteinic adsorption property were shown in Table 1.

[0031] [Example 3 of a comparison] While silicic-acid concentration agitated No. 3 sodium-silicate water-solution 20L which is 19 w/v%, and sulfuric-acid 3.3L of 12 normality to water 50L beforehand warmed at 60 degrees C, it applied to coincidence for 30 minutes, and added. pH under addition was 4-6. pH of a slurry was adjusted to 4 after addition termination, and 200 degrees C was heated for 60 minutes in the autoclave. After cooling, it filtered and washed and re-distributed in water. After readjusting pH to 4.0, the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification. The physical-properties value of the obtained silica and the proteinic adsorption property were shown in Table 1.

[0032]
[Table 1]

物性値	実施例		比較例		
	1	2	1	2	3
平均粒径（μm）	6.0	10.0	6.8	5.5	7.6
5%スラリーのpH	5.8	6.2	5.7	6.0	6.4
比表面積（m^2／g）	425	410	150	409	205
細孔分布	図1	図1	図1	図1	図1
全細孔容積（ml／g）：Vtotal	1.10	1.06	0.80	0.43	0.95
細孔容積（細孔ピーク半径±1nm, ml／g）：Vc*	0.54	0.65	0.03	0.05	0.14
Vc／Vtotal（%）	49	61	4	12	15
細孔ピーク半径（nm）**	4.1	4.1	1.1	1.1	11.4
ΔVp／ΔRpの最大値（mm^3／nm・g）	410	520	40	80	100
平均細孔半径（nm）	5.2	5.2	10.7	2.1	8.0
吸油量（ml／100g）	155	160	235	230	205
トリプシンインヒビター（分子量20100）の吸着率（%）***	15	20	30	23	10
カルボニックアンハイドラーゼ（分子量30000）の吸着率（%）***	70	64	36	42	52
牛血清アルブミン（分子量69000）の吸着率（%）***	26	21	34	40	44
カタラーゼ（分子量230000）の吸着率（%）***	20	35	60	45	60

＊細孔ピーク半径が2nm以下の場合は1.1nm以上の範囲で該当する範囲の細孔容積とした。

** ΔVp／ΔRp値が最大値を示す細孔半径

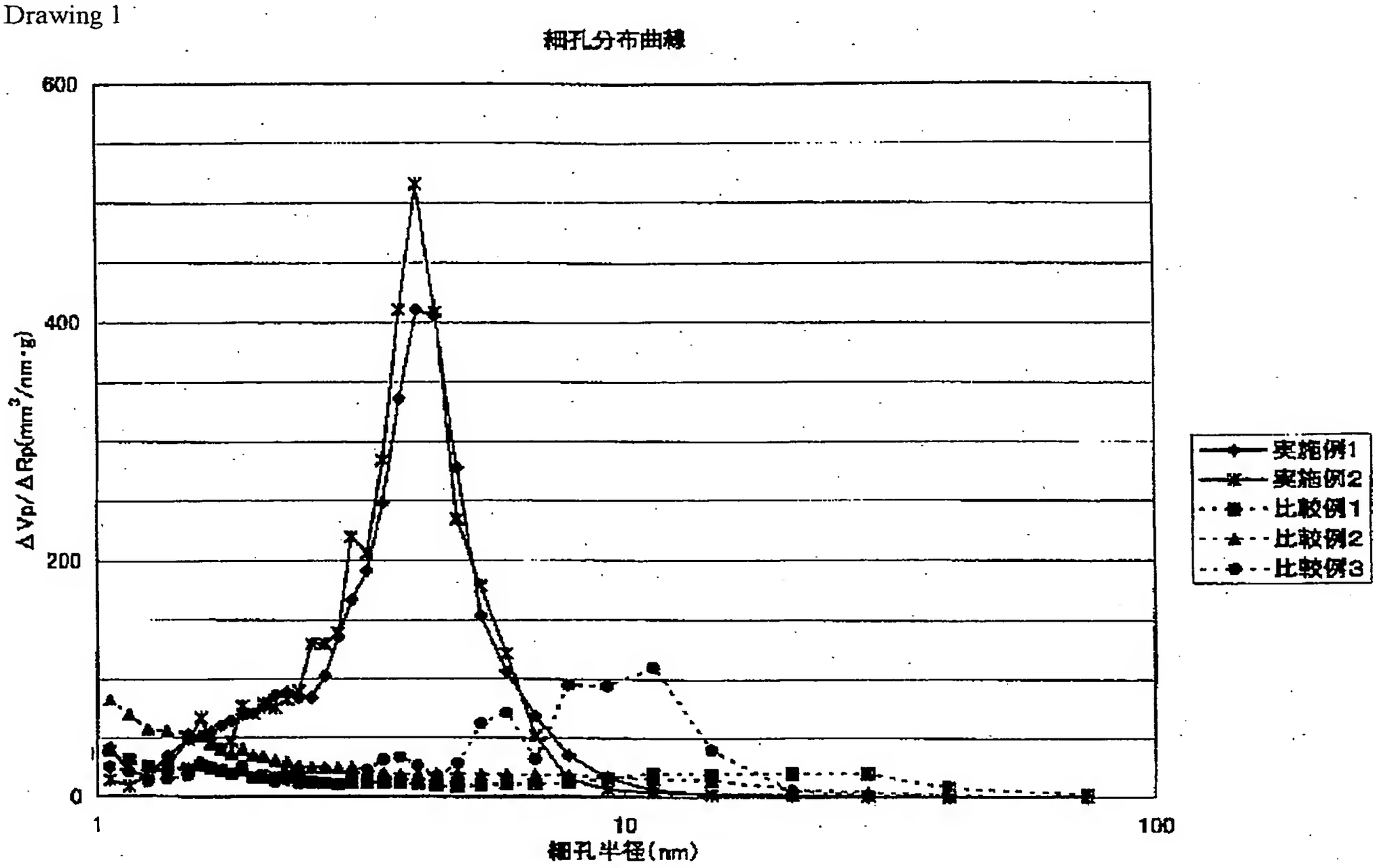
*** 図2参照

[0033] It was admitted that the silicon dioxide of an example showed a specific adsorption property to the matter (protein) which has specific molecular weight so that it might see at the above-mentioned result, especially the result of drawing 2 .

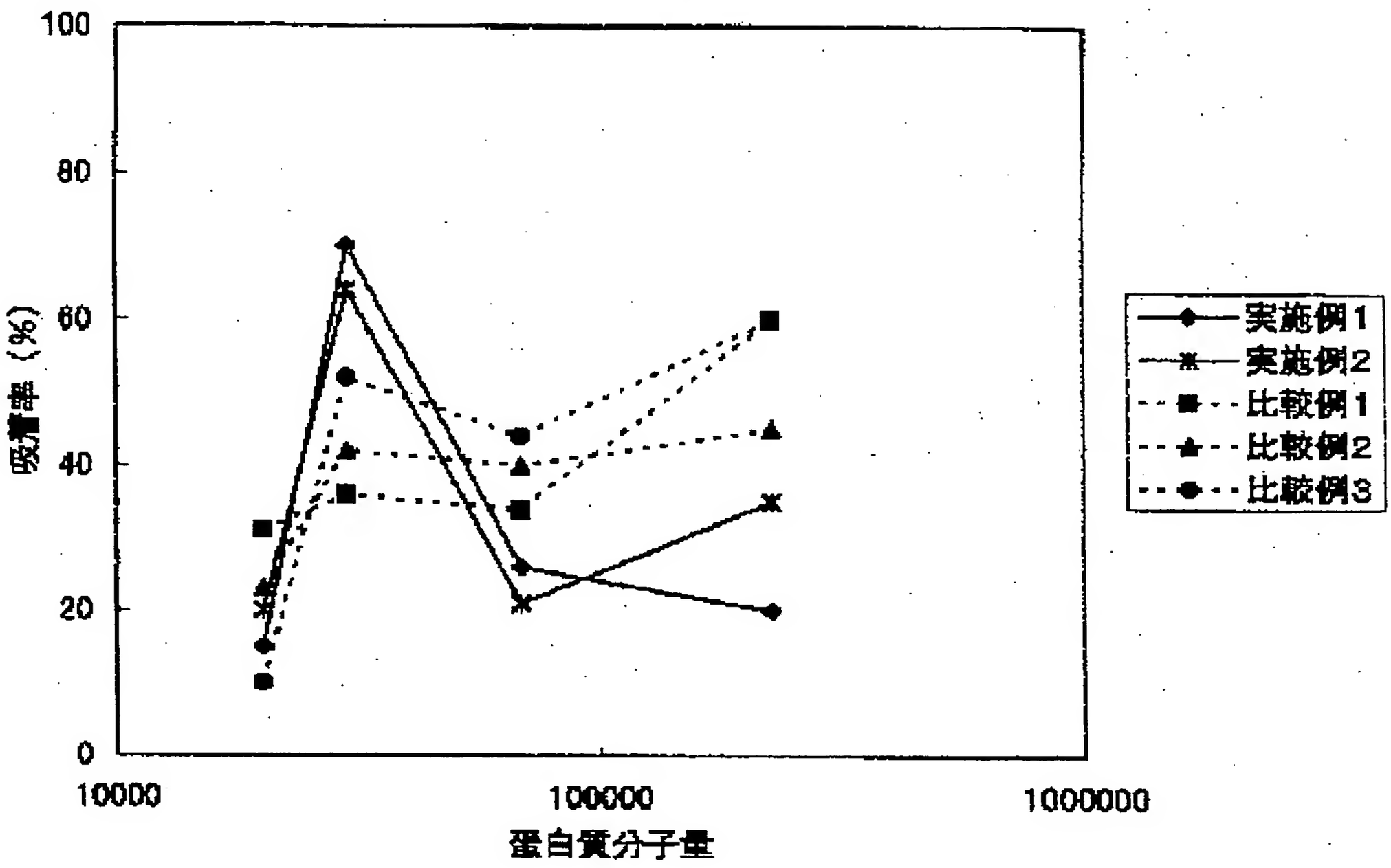
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the pore distribution map of an example and the example of a comparison.
[Drawing 2] It is the graph which shows the adsorption engine performance to the various protein of an example and the example of a comparison.

Drawing 1



Drawing 2


蛋白質吸着特性
100
80
60
40
20
0
吸着率（%）
10000
100000
1000000
蛋白質分子量
実施例1
実施例2
比較例1
比較例2
比較例3

CLAIMS

[Claim(s)]

[Claim 1] The silicon dioxide whose rate of the pore volume which is equivalent to the range of **1nm pore peak radius (pore radius delta ****/delta Rp indicates maximum to be) to total pore volume it has the maximum of a delta ****/delta Rp value (however, **** pore volume and Rp pore radius) in 10nm or less of pore radii, and the maximum of the delta ****/delta Rp value is more than 100mm3/nm-g in a pore distribution curve, and is 20% or more of total pore volume.

[Claim 2] The silicon dioxide according to claim 1 whose rate of the pore volume which is equivalent to the range of **1nm pore peak radius (pore radius delta ****/delta Rp indicates maximum to be) to total pore volume it has the maximum of a delta ****/delta Rp value (however, **** pore volume and Rp pore radius) in 3-8nm of pore radii, and the maximum of the delta ****/delta Rp value is more than 200mm3/nm-g in a pore distribution curve, and is 20% or more of total pore volume.

[Claim 3] The silicon dioxide according to claim 2 whose rate of the pore volume which is equivalent to the range of **1nm pore peak radius (pore radius delta ****/delta Rp indicates maximum to be) to total pore volume it has the maximum of a delta ****/delta Rp value (however, **** pore volume and Rp pore radius) in 3-5nm of pore radii, and the maximum of the delta ****/delta Rp value is more than 400mm3/nm-g in a pore distribution curve, and is 40% or more of total pore volume.

[Claim 4] The silicon dioxide according to claim 1, 2, or 3 whose specific surface area is 300-500m2/g and whose pore volume is 0.8 - 1.4 ml/g.

[Claim 5] Claim 1 whose mean particle diameter is 1-30 micrometers thru/or the silicon dioxide of four given in any 1 term.

[Claim 6] The silicon dioxide according to claim 5 whose mean particle diameter is 5-20 micrometers.

[Claim 7] Claim 1 whose pH of a 5-% of the weight slurry is eight or less thru/or the silicon dioxide of six given in any 1 term.

[Claim 8] Claim 1 whose oil absorption is 150ml / 100g or more thru/or the silicon dioxide of seven given in any 1 term.

[Claim 9] Claim 1 obtained when silicic-acid concentration made the alkali-metal silicate water solution and mineral acid below 10 weight / capacity % react thru/or the silicon dioxide of eight given in any 1 term.